PL-10

OUR JOURNEY WITH AZIRIDINE, AZIRINE AND 4-HYDROXYCOUMARIN

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Abstract. We have observed that the allylic zinc halide under identical reaction conditions acts in different modes for different electrophiles. For Ts-aziridines the halide part of the allylic halide has been introduced as a nucleophile and for the carbonyl compounds the simple allylation reaction occurred. To the best of our knowledge this is the first report where the allylic zinc halide is the source of halide as nucleophile.1 In another reaction of aziridine an efficient and new approach has been developed to synthesize bis(β,β′-dialkoxy carbonyl) derivatives through the reaction between N-tosylaziridines and malonate esters under ambient air using tBuOK in DMSO solvent. This reaction offers a broad substrate scope, metal-free synthesis, excellent regioselectivity, easily accessible reactants, and simple operation. A gram-scale synthesis demonstrates the potential applications of the present method.2

For another heterocycle 2H-azirine a visible-light-promoted regioselective C(sp3)-H coupling reaction with (diacetoxy)iodobenzene (PIDA) has been achieved using a catalytic amount of rose bengal as an organophotoredox-catalyst at ambient temperature under aerobic conditions. A variety of acyloxylated azirines with various functional groups have been synthesized in moderate to good yields.3 We have also reported a rapid and efficient approach has been developed to synthesize N-trifluoroacetylated α-amino ketone derivatives through the reaction between 2H-azirines and trifluoroacetic acid (TFA) under ambient air at room temperature within 10 minutes. This protocol is equally effective to synthesize N-formylated α-amino ketone and N-hydroxymethylated formamide derivatives.4

1-Butane sulfonic acid-3-methylimidazolium tosylate, [BSMIM]OTs is found to be a remarkable catalyst for the tandem cyclization of 4-hydroxycoumarin with chalcones for the syntheses of pyrano[3,2-c]coumarins under solvent-free conditions. The developed protocol is applicable for the construction of biologically important pyranocoumarins from easily accessible chalcones having various substituents. This reaction possibly proceeds through Michael addition followed by cyclization. The feasibility of the catalyst recycling is also demonstrated.5 The unique nucleophilic character of carbonyl oxygen of 4-hydroxycoumarin has been observed by the BF3·OEt2 catalyzed reaction of 4-hydroxycoumarin and alkynes. This protocol is operationally very simple and has much potential for the synthesis of heteroarylated vinyl ethers from basic chemicals.6 Te details for these will be disccussed in the talk.

References

1. S. Samanta, S. Santra, R. Chatterjee and **A. Majee**, *Org. Bio. Mol. Chem.* **2020,** *18,* 551.
2. R. Chatterjee, S. Samanta, A. Mukherjee, S. Santra, G. V. Zyryanov, **A. Majee**, *Tetrahedron Lett.* **2019**, 60, 276.
3. A. De, S. Santra, A. Hajra, G. V. Zyryanov and **A. Majee,** *J. Org. Chem.* **2019,** *84*, 11735.
4. A. De, S. Santra, G. V. Zyryanov and **A. Majee,** Org. Lett. **2020**, 22, 2936.
5. S. Samanta, S. Santra, R. Chatterjee and A. Majee, Org. Bio. Mol. Chem. 2020, 18, 551.
6. R. Chatterjee, S. Santra, G. V. Zyryanov, A. Majee, Synthesis, 2019, 51, 2371.

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